

## **Temporal and Spatial Scales of Terrestrially-derived Particulate and Dissolved Material in the Penobscot River System: Quantifying Conserved and Non-conserved Optical Properties and Transformations Within the Estuary**

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### **LONG-TERM GOALS**

Coastal waters represent the commingling of offshore marine and terrestrial surface source waters and therefore are naturally complex and variable. Our long term goal is to establish observational and modeling approaches to predict sources and scales of variability in the source waters, particularly those related to land use activities in upstream watersheds, from observations and measurements in the coastal waters.

### **OBJECTIVES**

Hydrologic optics provides an approach to characterizing physical and biogeochemical processes in aquatic systems over a range of time and space scales. The linkage between observations of the inherent optical properties (IOPs; absorption, scattering and fluorescence) and the geophysical properties lie in the establishment of robust optical proxies and the quantification of the temporal and spatial scales over which these proxies remain conservative in their properties. Our objectives are to identify and quantify specific optical and chemical characteristics of the colored particulate and dissolved fractions originating in the Penobscot River system that are associated with defined land use activities (land use proxies), and to determine the scales of variability over which these proxies can be detected both temporally (i.e. seasonal and episodic events) and spatially (from the source into coastal waters).

### **APPROACH**

Our approach combines high resolution temporal and spatial hydrographic and optical observations from moored, surface underway and profiling platforms with chemical characterization of the organic and inorganic, particulate and dissolved carbon and nitrogen pools that originate in the sub-watershed drainage basins of the Penobscot River System and flow through Penobscot Bay estuary into the coastal waters of the Gulf of Maine. Our approach is to (1) identify optical proxies for biogeochemical

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parameters, including quantifying the time and space scales of conservative behavior; (2) apply these proxies to high-resolution time and space optical observations to compute concentration and flux of riverborne material into the estuary and coastal systems; (3) compare models for conserved behavior with observations to identify zones and times of non-conserved behavior; (4) elucidate transformation processes at these locations/times; (5) quantify impacts of land use on the biogeochemical properties of the coastal ocean with the goal to predict responses to climate induced hydrologic forcing.

## WORK COMPLETED

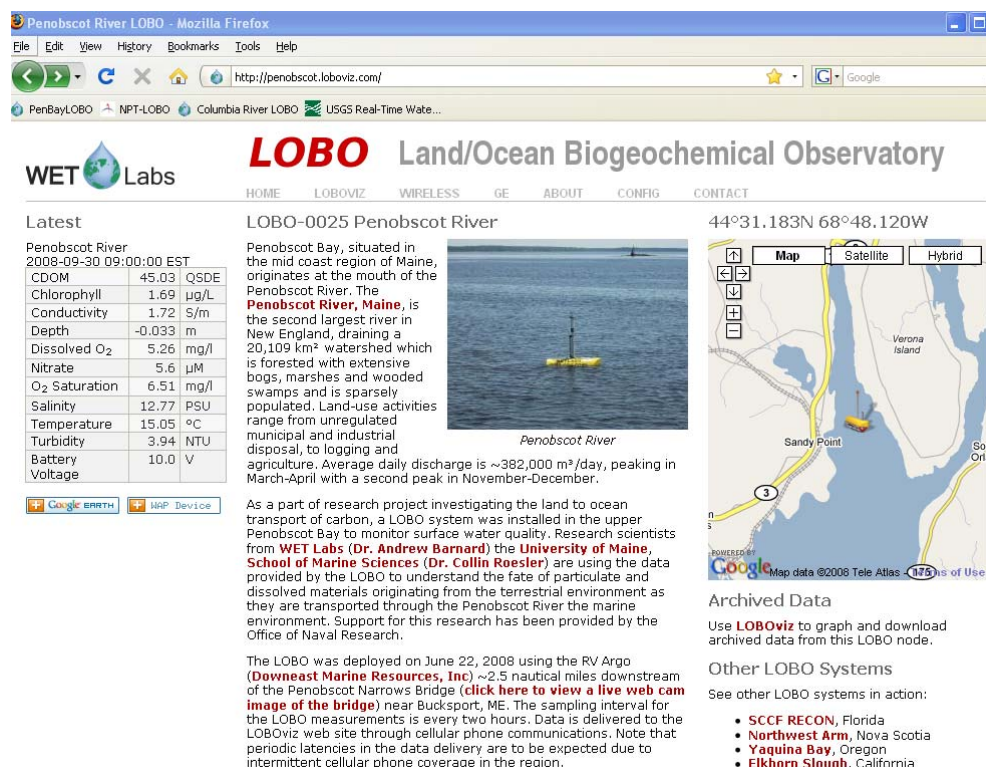
Over the past year, we have focused on maintaining a small turn-key surface water quality monitoring system, termed the Land/Ocean Biogeochemical Observatory (LOBO), in upper Penobscot Bay. This mooring is equipped with sensor packages for physical (temperature, conductivity, pressure, dissolved oxygen) and optical ( $F_{chl}$  and  $F_{cdom}$  and backscattering) and chemical (nitrate) properties in the upper 1 meter. While efforts conducted in the original funding were able to provide information as to the optical proxy temporal variability in the freshwater (river) and coastal endmembers (GoMOOS mooring F), we have not been able to fully resolve these time scales within the reactive region of the bay near 15 psu salinity. In the summer of 2008, we installed the LOBO mooring system (Figure 1) to monitor the hourly variability in these parameters in order to understand how the optical proxies vary as a function of tides, episodic events, river runoff, and season. The LOBO system uses a cellular phone to transmit data to shore. A real-time data and information web site interface (Figure 2) was also developed, and all data is publically available through this web site (<http://penobscot.loboviz.com>). We also equipped this mooring with a particle size distribution sensor (LISST provided by CSR) to improve our understanding of the temporal variability in the particulate fraction. Data from the LISST instrument however, are not available on the web interface, as the instrument is autonomously recording data.



**Figure 1. Left panel: Picture of the Penobscot Bay LOBO monitoring system on deck of the RV Argo after recovery on June 22, 2009. Middle panel: LOBO system after servicing on June 22, 2009 ready to deploy. Sampling instrumentation; WET Labs WQM, FLCDS, Satlantic ISUS, and Sequoia LISST are mounted on the frame below the yellow flotation. Right panel: Map of the upper Penobscot Bay with the deployment location of the LOBO mooring shown as a yellow icon. The mooring is located south of the town of Bucksport, ME. Map courtesy of Google Earth.**

The LOBO system was deployed in the upper Penobscot Bay (Figure 1) on 22 June 2008. The system was programmed to sample every two hours to conserve on battery power. The LOBO platform was initially serviced for normal maintenance (battery replacement, cleaning, sensor calibration, etc) on

August 25-27, 2008. After servicing, the LOBO system was redeployed at the same location on August 27, 2008. Due to a battery failure, the LOBO system ceased operation on October 23, 2008, and was subsequently recovered. We decided not to redeploy the mooring for the winter season due to high risk of the mooring breaking free during the Penobscot River ice out season. The mooring system was returned to WET Labs for a complete maintenance and servicing in preparation for the spring 2009 redeployment.



**Figure 2. Penobscot Bay LOBO information web site home page. All data from the mooring is freely available through this site (<http://penobscot.loboviz.com>).**

The LOBO mooring was successfully redeployed from the R/V Argo Maine on March 20, 2009. A larger capacity battery pack (102 AH) was installed for the deployment to extend the deployment period before servicing. We serviced the LOBO mooring on June 22, 2009, which included normal cleaning, data downloading, instrument calibrations, and battery replacements. The LISST instrument (maintained and operated by Dr. Roesler) was also serviced including downloading of the stored data. We redeployed the LOBO mooring at the same location on June 23 (Figure 1). The sampling interval was changed to hourly (previous deployments had been every two hours) to aid in capturing the tidal scale of variability. The LOBO system operated successfully until June 30, when we first noticed abnormal battery pack power supply variations and loss of nitrate data. To conserve on battery power, we autonomously changed the sampling scheduled back to every two hours for the ISUS nitrate sensor. The LOBO suffered a subsequent complete battery failure on July 9, resulting in loss of data. We were able to organize an abbreviated servicing for the LOBO system, wherein the failed battery pack was removed and a new smaller capacity (51 AH) battery pack was installed on the LOBO mooring on July 21, 2009. Due to the smaller capacity battery pack used, the sampling schedule was set for hourly

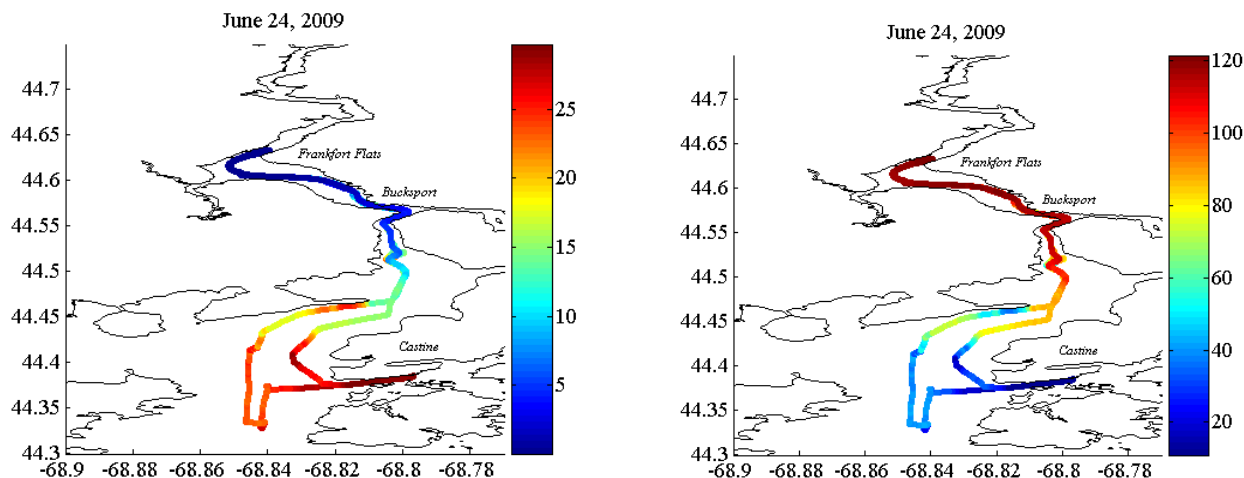
sampling for all instruments with the exception of the ISUS nitrate sensor which was set to every two hours. The LOBO continues to sample on this schedule as of the time of writing this report. A routine maintenance and servicing of the system is scheduled for October 15, 2009. We intend to continue the deployment until mid December 2009 at which time the mooring will be recovered for its complete annual servicing and over wintering.

Over the past reporting period, we have conducted one survey during June 23-24, 2009, mapping the spatial distributions of optical and physical parameters (Figure 3). The field survey was conducted from the RV Argo Maine with our in line sampling system and which was augmented with a hyperspectral absorption/attenuation meter (AC-S) to provide additional spectral resolution in mapping the key optical parameters of the system. A profiling system equipped with spectral attenuation and absorption meters, backscattering sensors, chlorophyll and CDOM fluorimeters, a CTD, and dissolved oxygen sensor was used to obtain the vertical distribution of dissolved and particulate materials along the salinity gradient through the lower Penobscot River and Bay. Water samples were collected for chlorophyll, spectral fluorescence and absorption, nutrients, particle size distributions, and dissolved organic carbon concentrations. During the June 2009 cruise, we also conducted a photobleaching experiment to characterize the dissolved organic transformations.

The survey focused on characterizing the key transition region (~5 - 25 PSU) in terms of the distributions and concentrations of dissolved and particulate materials near the LOBO location during an ebb tidal cycle. Most of the operations were conducted within a 2 mile radius of the LOBO mooring location, though each day did also include surveying the surface waters from Castine, ME to the freshwater endmember north of the Frankfort Flats region (Figure 3). Profiling operations were intensively conducted near the LOBO mooring site to characterize the optical property changes over the ebb tidal cycle.

We also conducted a CDOM photobleaching/photoxidation experiments by first collecting Penobscot River surface water (salinity <1.0 psu) in the early morning of June 23. Four treatments for the experiment were prepared from the river sample collected water: unfiltered dark (control), unfiltered light, filtered dark, unfiltered light. These separate the abiotic from biotic changes (filtered vs unfiltered) that occur in the light and dark. The samples were placed in coolers (closed for the dark, and open for the light) both of which were circulated with ambient surface waters throughout the day. Hourly samples were collected to measure changes in the absorption spectrum, pH, and DOC concentration. Samples were incubated throughout the morning and afternoon of June 23.





**Figure 3.** *Spatial distributions of surface salinity and CDOM fluorescence within the upper Penobscot Bay region obtained during the June 23-24, 2009 field survey using an inline sampling system installed on the RV Argo. Left panel shows the surface distributions of salinity obtained on 24 June 2009. Right panel shows the surface distributions of CDOM obtained on 23 June 2009. Color bars show the salinity and CDOM concentrations (ppb QSE) for each panel.*

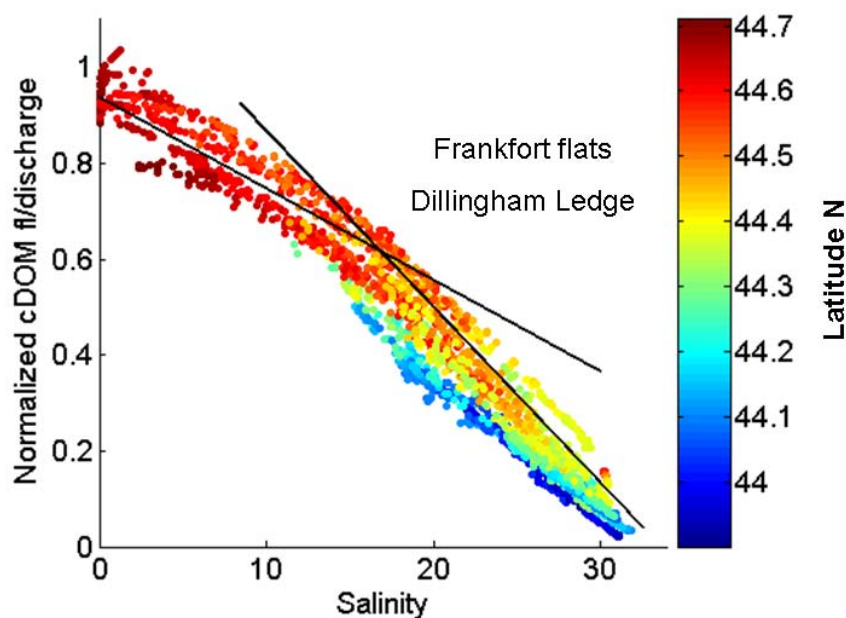
## RESULTS

The optical property which shows the best correlation with salinity is cDOM fluorescence, regardless of sampling period. Our previous results have shown that  $F_{\text{cDOM}}$  is an excellent proxy for DOC concentration within the Penobscot River. Plotting the  $F_{\text{cDOM}}$  surface data normalized to the freshwater endmember  $F_{\text{cDOM}}$  maximum against surface salinity from the transects we have conducted throughout this project (Figure 4) has demonstrated (1) how concentration is discharge dependent and (2) the non-conserved behavior within the estuary. In order to elucidate how much of the seasonal variability in the cDOM fluorescence is due to changes in the volume transport of the Penobscot River, we normalized the cDOM fluorescence data by the discharge measured at the USGS gage station at Eddington, ME for each sampling period. When normalized to discharge, the seasonal trend in cDOM delivery from the river entering into the bay show that the concentration is correlated with discharge. Several studies have shown strongly conservative (linear) relationships between dissolved absorption at 412nm and/or cDOM fluorescence and salinity for different freshwater inputs, indicating that this proxy can be used as a simple water mass tracer (Coble et al 1998; Twardowski and Donaghay 2001; Blough and Del Vecchio, 2002; Coble et al 2004). However, it is noteworthy that all sampling periods show pronounced non-conservative behavior, indicating that either transformations of the fluorescent DOC are occurring (i.e. that non-fluorescing matter from the river is being transformed to fluorescing matter) or that there is a source of new fluorescent cDOM within the estuary.

There appears to be a distinct change in slope at approximately 15 psu, indicating a source of fluorescent dissolved matter. However, when normalizing the cDOM delivery observations ( $F_{\text{cDOM}} / \text{discharge}$ ) by the cDOM delivery in at the low river station ( $F_{\text{cDOM}} / \text{discharge}$  near the Eddington), the data collapses onto a single curve and the location of slope change is not a specific salinity value (which would imply a chemical process) but a specific geographic location (i.e. Frankfort Flats) suggesting that the transformation processes are likely physically mediated. Analysis of particle

properties, from discrete and in situ observations, in this region show enhanced particle concentrations at all times of the year. It is uncertain if these particles are the result of tidal mixing and resuspension, chemical precipitation or aggregation. However, it is clear that this is a hot spot with respect to DOC transformation and that those transformations are likely to involve significant interaction with particulate matter.

Every survey has demonstrated that the apparent site of non-conservative behavior in DOM is co-located with enhance particle concentrations, and that the transformation processes or input sources appear to be determined geographically and not at a certain salinity. This leads us to question the role of particulate matter in the transformation of the DOM, and to the driving mechanisms (river discharge, tides, nutrients, etc) that lead to these transformations. Our work to date as lead us to identify and quantify the magnitude, location, and timing of the non-conservative behavior in the particulate and dissolved organic matter and optical pools in the Penobscot River system. While we have discerned that the non-conservative behavior appears to be spatially and temporally coherent, we have not be able to identify the exact processes responsible for the non-conserved behavior or resolve the direct linkages between the particular and dissolved pools. The two specific questions we are seeking to address are 1) what are the controlling mechanisms for the DOC proxy changes (particle/bacterial/chemical mediation), and 2) what is the temporal variability in these transformations (changes with season, tidal mixing, DOC composition and delivery).



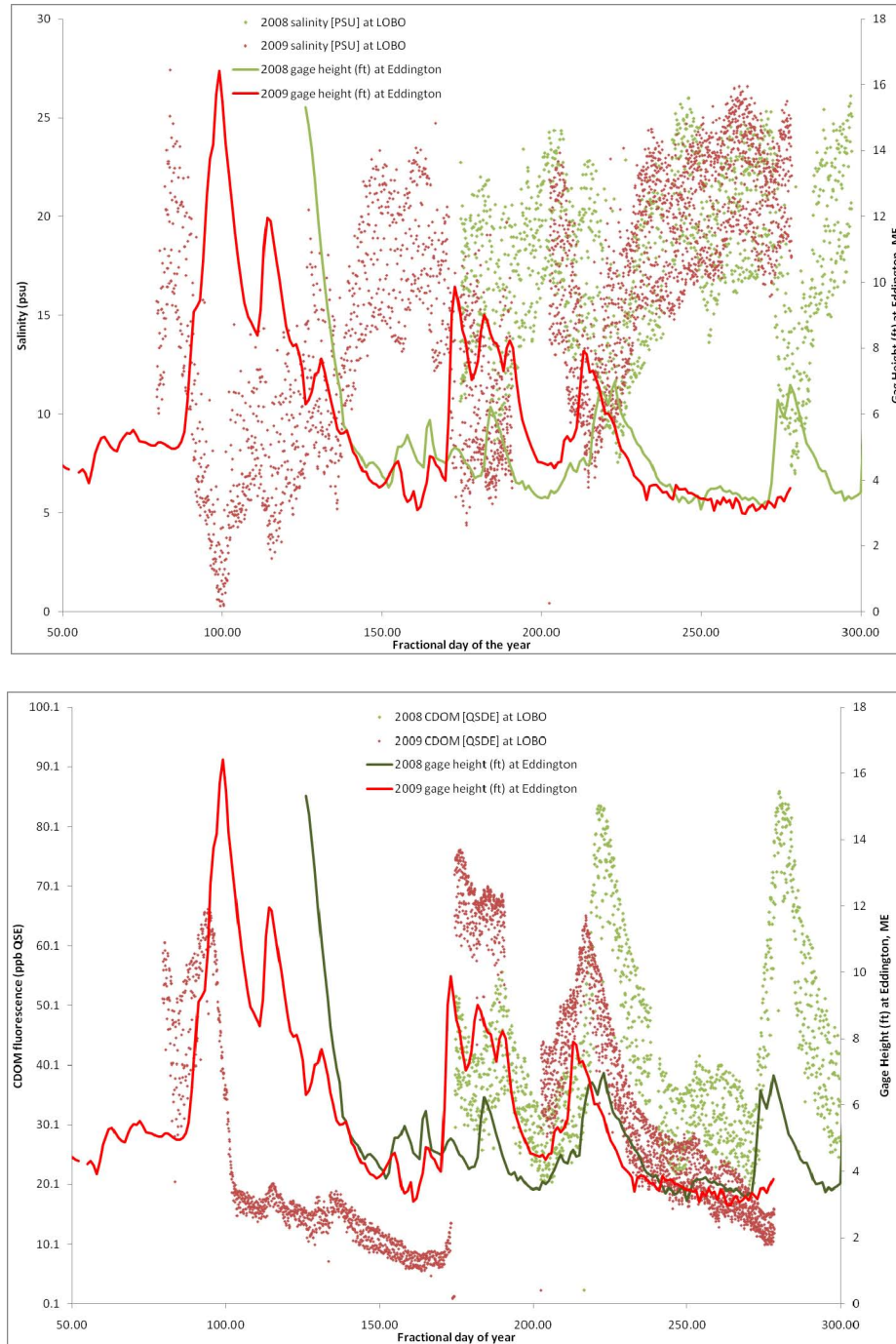
**Figure 4.** Surface distributions of salinity versus CDOM fluorescence normalized to the maximum and to the Penobscot river discharge (at Eddington, ME based on USGS data) throughout the lower Penobscot River and Penobscot Bay region. Data shown are from eight separate time periods spanning 3 years. Colors indicate latitude where data was obtained (see colorbar). Solid black lines indicate the two linear sections of the relationship. The intersection of these two lines typically occurs in the region near Bucksport, ME (from Frankfort Flats down to Stockton Springs, ME).

To assist in addressing these questions, we deployed a LOBO mooring on 22 June 2008 to monitor the temporal variability in surface distributions of temperature, salinity, dissolved oxygen, chlorophyll, CDOM, particles, and nitrate concentrations. Our objective is to operate the LOBO mooring from the spring through the fall only, due to the high risk of the mooring breaking free during the winter months due to heavy ice flow down the Penobscot River. The 2008 deployment was unfortunately shortened due to battery pack failure (recovered in late October 2008). The LOBO 2009 deployment is ongoing, and will extend from mid March through early December. Servicing and maintenance of the mooring is relatively easy (servicing typically accomplished in one day), and with the integrated anti-fouling systems of the LOBO mooring system, 3 month service intervals are sufficient to maintain good data quality. The exception has been with the optical nitrate measurements, which are typically limited to 4-6 weeks before fouling severely degrades the measurement quality.

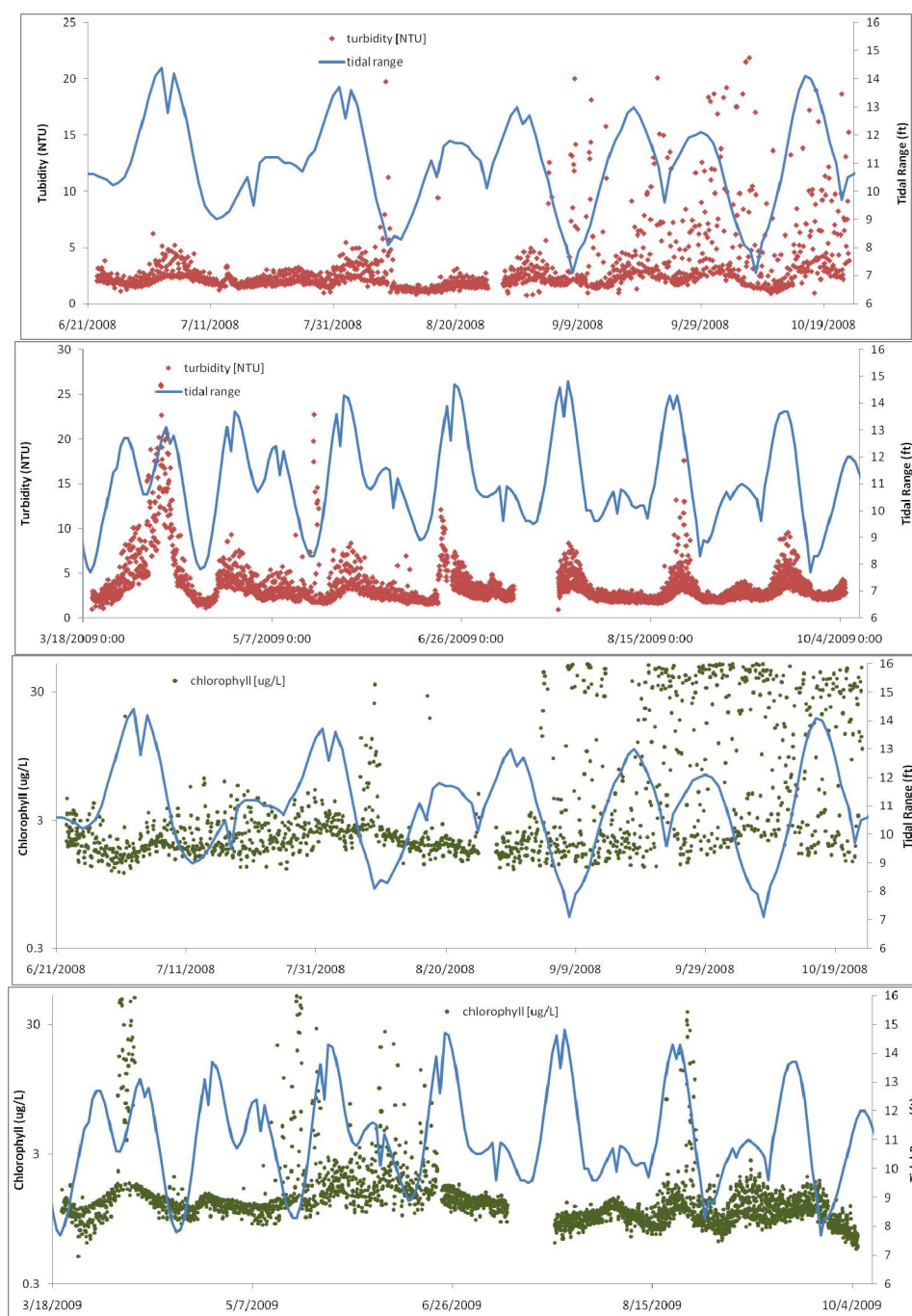
Observations from the LOBO mooring have highlighted the dual importance of the tidal fluctuations and river discharge in the distributions of the dissolved and particulate materials. In particular, the observations from the LOBO system have shown that there is strong tidal influence on the daily range of surface salinity and CDOM concentration (i.e. the region is a sight of active tidal mixing), and that the longer term average (days to weeks) surface salinity and CDOM is highly correlated with discharge from the Penobscot River (Figure 5). The 2008 and 2009 summer to fall periods showed remarkable similarity in the salinity and CDOM fluctuations associated with periodic fall storms flushing water into the lower Penobscot River. Thus the daily to seasonal scales of variability in dissolved materials in the upper Penobscot Estuary is predominately associated with the Penobscot River and associated watershed flushing, and is actively mixed in the Estuary with coastal dissolved materials by the tides.

Data observations from the LOBO mooring have also provided insight into the controlling mechanisms on the particulate material temporal variability in the upper Penobscot Estuary. LOBO data collected during both 2008 and 2009 show that the largest increases in turbidity occur during periods of the largest tidal range (i.e. spring tides), indicating that processes of bottom sediment resuspension strongly control the water clarity in the region (Figure 6). We also find that the chlorophyll variability is weakly correlated with the tidal range (Figure 6) and river discharge.



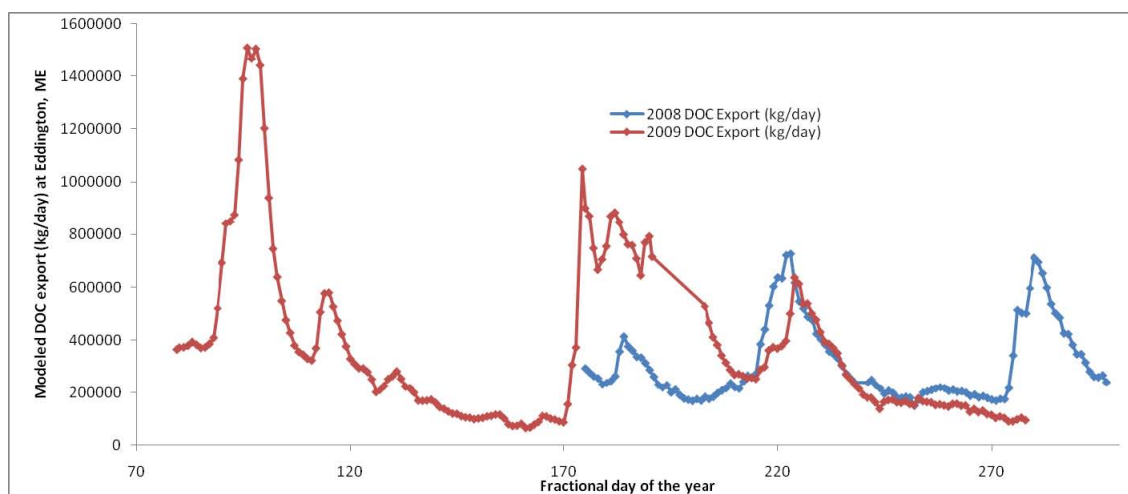


**Figure 5. Surface data from the LOBO mooring installed in the upper Penobscot Bay region for the 2008 and 2009 periods. Top panel shows the surface salinity observations from the LOBO mooring in 2008 (green circles) and 2009 (red circles). Also shown is the river gage height data (courtesy of USGS) at Eddington, ME from 2008 (green line) and 2009 (red line). Bottom panel shows the surface CDOM fluorescence observations along with the gage height data for 2008 and 2009 (symbols and colors same as top panel). Note the strong tidal periodicity in salinity and the strong correlation between the river height and CDOM concentration.**



**Figure 6. Surface distributions of turbidity and chlorophyll obtained at the LOBO station in the upper Penobscot Estuary for the 2008 and 2009 periods. Top two panels show the turbidity (red circles) data from the LOBO along with the daily tidal range (blue lines) for the 2008 and 2009 seasons. Bottom two panels show the chlorophyll observations (green circles) from the LOBO system for the 2008 and 2009 periods along with the tidal range. Note that the variability in the particulate materials (as inferred from turbidity and chlorophyll) at the LOBO site is strongly associated with lunar tidal cycles, in particular the turbidity increases are consistently associated with the spring tides.**

As a part of a related study to examine the dissolved carbon flux from the Penobscot River to the coastal regions, we have also developed a model to predict the DOC flux from the Penobscot River using the observations obtained from the LOBO mooring. The model is based on the CDOM fluorescence to DOC concentration relationship developed over 4 years of field sample collections in the Penobscot River and Bay system, and the surface CDOM fluorescence to salinity relationships observed over 4 years of field surveys (Figure 4). Surface observations of CDOM fluorescence and salinity from the LOBO system along with the river discharge (modeled from the USGS river gage) are used to estimate the DOC daily loading at Eddington, ME (Figure 7).



**Figure 7. Modeled DOC flux at Eddington, ME in the Penobscot River using data obtained from the LOBO mooring and the USGS river gage height information.**

## IMPACT/APPLICATIONS

The results of this study will contribute to identification of optical and biogeochemical signatures associated with specific land use activities, and quantification of the tracer potential of those signatures through the river and estuarine system to the coastal environment. The application of this approach is the capability for determining changes in terrestrial land use from autonomous observations in the river and coastal waters. Identifying the conservative and nonconservative optical and chemical variability in the dissolved and particulate fractions of river inputs will also contribute to the development of coastal and watershed models of carbon flux. The high temporal resolution data obtained in this study will allow for quantification of this variability on time scales of hours to months, covering a range of scales from daily to seasonal to interannual and including episodic events. While the focus of this study does not address the specific transformations operating within a riverine impacted regions, these results will be useful in aiding our understanding of the relevant biogeochemical processes operating in the coastal margins influenced by riverine inputs by determining the appropriate temporal and spatial scales of optical and chemical variability that are conserved through the system.

## TRANSITIONS

The USGS Augusta, ME office and the Penobscot Indian Nation have shown a strong interest in the observations and water quality monitoring capabilities of the LOBO mooring system. Satlantic and WET Labs are working with these groups to evaluate using a LOBO system in the upper Penobscot

River region to monitor the impacts of biogeochemical variability due to anthropogenic changes in the system associated with industrial processing plants. The LOBO mooring deployed in upper Penobscot Bay through this project is providing real-time bio-optical and physical data, and all data is available through the LOBO web interface (<http://penobscot.loboviz.com>). We are tracking the web site traffic and data downloads to understand the utility of these data outside of the research community.

## RELATED PROJECTS

1. Both C. Roesler and A. Barnard are Co-PIs on a NASA sponsored multi-investigator research project examining the variability in fluxes of dissolved and particulate organic carbon from terrestrial sources to the Gulf of Maine via major rivers, and their subsequent fate within the Gulf of Maine. This work is specifically focusing on the impacts of riverine dissolved and particulate loading to the carbon cycle of coastal and offshore systems. Our ONR project is highly complementary to this project, as it is providing a better understanding of the variability in the concentration and composition of the Penobscot River dissolved and particulate materials and its subsequent delivery to the coastal and offshore regions.
2. Dr. Barnard is involved with the Coastal Margin Observation and Prediction (CMOP) Science and Technology Center (Oregon Health and Sciences University, NSF) to develop, deploy, and maintain a Land/Ocean Biogeochemical Observatory (LOBO) node for the lower Columbia River. Similar to the LOBO system used in the Penobscot, the Columbia River node includes the same sensing suite (<http://columbia.loboviz.com>). The goals of this project are to understand the role of large sediment fluxes on the dissolve organic materials. This mooring will also integrate an in situ phosphate sensor over the next year to more fully characterize the nutrient variability within the lower Columbia River.

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